

**SUBSTRATE COATED WITH A DIELECTRIC LAYER AND PROCESS AND
INSTALLATION FOR MANUFACTURING IT**

5 The present invention relates to the field of dielectric-based thin-film coatings, especially of the metal oxide, nitride or oxynitride type, which are deposited on transparent substrates, especially glass substrates, using a vacuum deposition technique.

 The invention relates to a coated substrate, to a manufacturing process, to an
10 installation for manufacturing and for applying the substrate and/or the process for producing glazing assemblies, especially double-glazing or laminated glazing assemblies, comprising at least one substrate according to the invention.

 For the purpose of manufacturing what are called "functional" glazing
assemblies, the usual practice is to deposit, on at least one of the substrates of which
15 they are composed, a thin-film layer or a thin-film multilayer, so as to give the glazing assemblies optical (for example antireflection) properties, properties in the infrared (low emissivity) and/or electrical conduction properties. Layers based on an oxide and/or nitride dielectric are frequently used, for example on either side of a silver layer or a doped metal oxide layer, or as an interferential layer in multilayers in which
20 low- and high-refractive index dielectrics alternate.

 Layers deposited by sputtering are reputed to be somewhat less chemically and mechanically resistant than layers deposited by pyrolithic deposition. Thus, the experimental technique of ion-beam-assisted deposition has been developed in which a layer is bombarded with an ion beam, for example an oxygen or argon ion
25 beam, which makes it possible to increase the density of the layer and its adhesion to the carrier substrate. This technique has for a long time been applicable only to very small sized substrates, owing to the problems posed in particular in terms of convergence between, on the one hand, the ion beam coming from a very localized source and, on the other hand, the particles resulting from the evaporation or sputtering of the target.
30

 Document EP 601 928 discloses a sequential treatment of the deposited layer, by firstly depositing a layer in a sputtering chamber and then bombarding this dielectric layer after it has been deposited with a "low energy" ion beam coming from a point source, with an energy allowing the sputtering of the layer under the

impact of the ions of the beam to be limited, typically of less than 500 eV and around one hundred eV.

This treatment is aimed essentially at increasing the physical and/or chemical durability of the layer, by densification of the layer, and makes it possible to achieve a lower surface roughness of the layer, favoring the subsequent "layering" of a layer subsequently deposited on top of it.

However, this treatment has the drawback of only being able to be carried out on a fully deposited layer.

Another drawback of this treatment is that it allows only densification of the layer thus treated and this densification causes an increase in the refractive index of the layer thus treated. The layers thus treated therefore cannot replace the untreated layers, because of their different optical properties, and mean that the multilayer systems, in which the material must be included, have to be completely redefined.

In addition, this treatment is not optimized for being carried out on a large substrate, for example for the production of an architectural glazing assembly.

Furthermore, this process is not at all compatible with the sputtering process, especially magnetically enhanced sputtering and preferably reactive sputtering in the presence of oxygen and/or nitrogen, especially because of the very different working pressures : at the time of this invention, the ion sources operated at pressures 10 to 100 times lower than the pressures used in the processes for sputtering, especially magnetically enhanced sputtering and preferably reactive sputtering in the presence of oxygen and/or nitrogen.

More recently, ion sources have been developed that are more compatible with processes for depositing thin films by sputtering, in particular by solving the problem of convergence of the particle beams and by improving the matching between the size and the geometry, on the one hand, of the cathode and, on the other hand, of the ion source. These systems, known as "linear sources", are described for example in documents US 6 214 183 or US 6 454 910.

Document WO 02/46491 describes the use of a source of this type for producing a functional silver oxide layer by sputtering using a silver target with bombardment by an oxygen ion beam. The ion beam is used to densify the silver material and convert it into a layer containing silver oxide. As a result of the densification, the silver oxide layer is capable of absorbing and/or reflecting a significant amount of the UV.

The object of the present invention is to remedy the drawbacks of the prior art and to provide novel thin-film materials that can be used to coat transparent substrates of the glass type, novel deposition processes and novel installations.

5 The invention relies on the fact that it is possible to deposit thin-film layers made of a dielectric, especially an oxide and/or nitride, with exposure to an ion beam by controlling the conditions so that the material of the final layer has a better degree of crystallization, much greater than the degree of crystallization of the material deposited conventionally, that is to say without subjecting the layer to at least one ion beam.

10 In this regard, the subject of the invention is a substrate, especially a glass substrate, as claimed in claim 1. The substrate according to the invention is coated with at least one dielectric thin-film layer deposited by sputtering, especially magnetically enhanced sputtering and preferably reactive sputtering in the presence of oxygen and/or nitrogen, with exposure to at least one ion beam coming from an ion source, and the deposited dielectric layer exposed to the ion beam is crystallized.

15 The term "crystallized" is understood to mean that at least 30% of the constituent material of the dielectric layer exposed to the ion beam is crystallized and that the size of the crystallites can be detected by X-ray diffraction, i.e. they have a diameter of greater than a few nanometers.

20 The ion beam used to implement the present invention is what is called a "high-energy" beam, typically having an energy ranging from around several hundred eV to several thousand eV.

Advantageously, the parameters are controlled in such a way that the dielectric layer deposited on the substrate by sputtering with exposure to the ion beam has a very low roughness.

25 The term "very low roughness" is understood to mean that the dielectric layer exposed to the ion beam has a roughness at least 20%, and preferably at least 50%, less than that of the same dielectric layer not exposed to the ion beam.

The dielectric layer exposed to the ion beam may thus have a roughness of less than 0.1 nm for a thickness of 10 nm.

30 Advantageously, the parameters may also be controlled in such a way that the layer has an index very much less or very much greater than the index of a layer deposited without an ion beam, but which may also be close to the index of a layer deposited without an ion beam.

Within the meaning of the present description, the term "close" implies an index that differs from the reference value by at most around 5%.

The invention also makes it possible to create an index gradient in the deposited layer.

5 In a variant, said layer thus has an index gradient adjusted according to the parameters of the ion source.

Advantageously, for at least some of the dielectric materials that can be deposited, whatever the index modification produced, the density of the dielectric layer deposited on the substrate by sputtering with exposure to the ion beam may be
10 maintained with a similar or identical value.

Within the meaning of the present description, a "similar" density value differs from the reference value by at most around 10%.

The invention applies in particular to the production of a dielectric layer made of a metal oxide or silicon oxide, whether stoichiometric or nonstoichiometric, or
15 made of a metal nitride or oxynitride or silicon nitride or oxynitride.

In particular, the dielectric layer may be made of an oxide of at least one element taken from silicon, zinc, tantalum, titanium, tin, aluminum, zirconium, niobium, indium, cerium, and tungsten. Among mixed oxides that can be envisioned, mention may in particular be made of indium tin oxide (ITO).

20 The layer may be obtained from a cathode made of a doped metal, that is to say one containing a minor element : as an illustration, it is common practice to use cathodes made of zinc containing a minor proportion of another metal, such as aluminum or gallium. In the present description, the term "zinc oxide" is understood to mean a zinc oxide possibly containing a minor proportion of another metal. The
25 same applies to the other oxides mentioned.

For example, a zinc oxide layer deposited according to the invention may have a degree of crystallinity of greater than 90% and especially greater than 95% and an RMS roughness of less than 1.5 nm and especially around 1 nm.

This zinc oxide layer deposited according to the invention may have a
30 refractive index that can be adjusted to a value of less than or equal to 1.95, especially around 1.35 to 1.95. Its density may be maintained at a value close to 5.3 g/cm³ and especially at a value of around 5.3±0.2 g/cm³, identical to the density of a ZnO layer deposited at low pressure, which is around 5.3 g/cm³.

Zinc oxide layers having a refractive index adjusted to a value of less than
35 1.88 and similar to this value may be obtained by setting the sputtering conditions

(especially the oxygen content of the atmosphere) so as to deviate slightly from the stoichiometry of the intended oxide so as to compensate for the impact of the ion bombardment.

5 The dielectric layer may also be made of silicon nitride or oxynitride. Such nitride dielectric layers may be obtained by setting the sputtering conditions (especially the nitrogen content of the atmosphere) so as to deviate slightly from the stoichiometry of the intended nitride, so as to compensate for the impact of the ion bombardment.

10 In general, the ion beam has the effect of improving the mechanical properties of the dielectric layer.

As a result of the ion bombardment, quantities of one or more bombarded species are introduced into the layer, in a proportion that depends on the nature of the gas mixture at the source and on the source/cathode/substrate configuration. As an illustration, a layer deposited under bombardment by an argon ion beam may
15 include argon with a content of around 0.2 to 0.6 at%, especially about 0.45 at%.

Generating the ion beam via an ion source that uses soft iron cathodes or cathodes of any other material, especially paramagnetic material, which are eroded during the process, may be responsible for the presence of traces of iron in the deposited layer. It has been confirmed that iron present with a content of less than
20 3 at% or less is acceptable as it does not degrade the properties, especially optical or electrical properties, of the layer. Advantageously, the deposition parameters (especially the substrate transport speed) are adjusted so as to have an iron content of less than 1 at%.

By preserving the usual optical properties, it is very easy to incorporate the
25 dielectric layers thus obtained into multilayers known for manufacturing what are called "functional" glazing assemblies, in particular using a silver-based metal functional layer.

Specific multilayers may be designed that incorporate a dielectric of index adjusted to a different value from the standard value.

30 Thus, the subject of the invention is a substrate coated with a multilayer in which a silver layer is deposited on top of said dielectric layer exposed to the ion beam. Another dielectric layer may then be deposited on top of this silver layer.

This configuration proves to be particularly advantageous when the lower dielectric layer is based on zinc oxide and/or tin oxide as they give rise to particularly
35 well oriented growth of the silver layer on the oxide layer, with improved final

properties. It is known that the presence of a zinc oxide layer beneath the silver has an appreciable influence on the quality of said silver layer. The formation of the silver layer on the zinc oxide layer deposited according to the invention results in a quite remarkable improvement.

5 In fact it is observed that the silver layer thus formed is better crystallized with an increase of 15 to 40% in the crystalline phase (diffraction from (111) planes) compared with the amorphous phase.

In this regard, the subject of the invention is also a process according to the invention for improving the crystallization of a silver layer deposited on a dielectric
10 layer, especially on a dielectric layer based on zinc oxide, in which said dielectric layer is deposited on the substrate by sputtering, especially magnetically enhanced sputtering and preferably reactive sputtering in the presence of oxygen and/or nitrogen, with exposure to at least one ion beam, preferably coming from a linear source. According to this process, at least one functional layer, especially one based
15 on silver, is deposited on said dielectric layer and said functional layer undergoes a crystallization step. The size of the crystallites of the silver layer can therefore be increased by around 15 to 40%, especially 30 to 40% (diffraction from (111) planes).

This is manifested by a reduction in the resistivity of the silver (which is directly related to the energy emissivity properties) or a reduction in the surface resistance
20 R_{\square} by at least 10%, for the same silver thickness, with an R_{\square} value of less than $6 \Omega / \square$, or even less than $2.1 \Omega / \square$, especially around $1.9 \Omega / \square$.

These substrates are thus particularly advantageous for producing low-emissivity or solar-controlled glazing assemblies, or else translucent elements with a high electrical conductivity, such as the screens for electromagnetic shielding of
25 plasma display devices.

In these substrates, another dielectric layer may be placed on top of the silver layer. It may be chosen based on the abovementioned oxides or nitrides or oxynitrides. The other layer itself may or may not be deposited with exposure to an ion beam.

30 The multilayer may include at least two silver layers or even three or four silver layers.

Examples of multilayers that can be produced according to the invention comprise the following sequences of layers :

... ZnO ⁽ⁱ⁾ / Ag /oxide such as ZnO ...
 ... Si₃N₄ / ZnO ⁽ⁱ⁾ / Ag / oxide such as ZnO ...
 ... Si₃N₄ / ZnO ⁽ⁱ⁾ / Ag / Si₃N₄ / (optionally an oxide) ...
 ... Si₃N₄ / ZnO ⁽ⁱ⁾ / Ag / Si₃N₄ / ZnO ⁽ⁱ⁾ / Ag / Si₃N₄ ...
 5 ... Si₃N₄ / ZnO ⁽ⁱ⁾ / Ag / Si₃N₄ / ZnO ⁽ⁱ⁾ / Ag / Si₃N₄ / (oxide)...

where ⁽ⁱ⁾ indicates that the layer is exposed to the ion beam and where a blocking metal layer may be inserted above and/or below at least one silver layer.

The substrate used could also be made of a plastic, especially a transparent plastic.

10 The subject of the invention is also a process for manufacturing a substrate as described above, i.e. a process for depositing a multilayer, in which at least one dielectric layer is deposited on the substrate by sputtering, especially magnetically enhanced sputtering and preferably reactive sputtering in the presence of oxygen and/or nitrogen, in a sputtering chamber, with exposure to at least one ion beam
 15 coming from an ion source. In the process according to the invention, the ion beam is created from a linear source and the refractive index of said dielectric layer exposed to the ion beam may be adjusted according to the parameters of the ion source.

The refractive index of the dielectric layer exposed to the ion beam may be decreased or increased relative to the index of this layer deposited without an ion
 20 beam.

Advantageously, for at least some of the dielectric materials to be deposited, whatever the index modification produced, the density of the dielectric layer deposited on the substrate by sputtering with exposure to the ion beam is maintained.

25 Exposure to the ion beam takes place in the sputtering chamber simultaneously with and/or sequentially after the deposition of the layer by sputtering.

The expression "simultaneously with" is understood to mean that the constituent material of the dielectric thin-film layer is subjected to the effects of the ion beam while it is yet to be completely deposited, that is to say that it has not yet
 30 reached its final thickness.

The term "sequentially after" is understood to mean that the constituent material of the dielectric thin-film layer is subjected to the effects of the ion beam when the layer has been completely deposited, that is to say after it has reached its final thickness.

In the variant with exposure simultaneously with deposition, the position of the ion source(s) is preferably optimized so that the maximum density of sputtered particles coming from the target is juxtaposed with the ion beam(s).

5 Preferably, to produce an oxide-based dielectric layer, an oxygen ion beam is created with an atmosphere containing very largely oxygen, especially 100% oxygen, at the ion source, whereas the atmosphere at the sputtering cathode is preferably composed of 100% argon.

10 In this variant, exposure to the ion beam takes place simultaneously with the deposition of the layer by sputtering. For this purpose, it is unnecessary to limit the ion energy as in the prior art ; on the contrary, an ion beam with an energy between 200 and 2000 eV or even between 500 and 5000 eV, especially between 500 and 3000 eV, is advantageously created.

15 The ion beam may be directed onto the substrate and/or onto the sputtering cathode, especially along a direction or at a non-zero angle with the surface of the substrate and/or of the cathode respectively, such that the ion beam juxtaposes with the flux of neutral species ejected from the target by sputtering.

20 This angle may be around 10 to 80° relative to the normal to the substrate, measured for example vertically in line with the center of the cathode, and vertically in line with the axis of the cathode when it is cylindrical.

 In the case of direct flux on the target, the ion beam coming from the source juxtaposes with the " racetrack " of the target created by the sputtering, that is to say the centers of the two beams, coming from the cathode and from the ion source respectively, meet at the surface of the substrate.

25 Advantageously, the ion beam may also be used outside the racetrack and directed toward the cathode, in order to increase the degree of use of the target (ablation). The ion beam can therefore be directed onto the sputtering cathode at an angle of ± 10 to 80° relative to the normal to the substrate passing through the center of the cathode, and especially through the axis of the cathode when it is cylindrical.

30 The source/substrate distance, in a sequential or simultaneous configuration, is from 5 to 25 cm, preferably 10 ± 5 cm.

 The ion source may be positioned before or after the sputtering cathode along the direction in which the substrate runs (i.e. the angle between the ion source and the cathode or the substrate is respectively negative or positive relative to the normal
35 to the substrate passing through the center of the cathode).

In a variant of the invention, an ion beam is created in the sputtering chamber using a linear ion source simultaneously with the deposition of the layer by sputtering, and then the deposited layer undergoes an additional treatment with at least one other ion beam.

5 The present invention will be more clearly understood on reading the detailed description below of illustrative but non-limiting examples and from figure 1 appended hereto, which illustrates a longitudinal sectional view of an installation according to the invention.

10 To manufacture "functional" glazing assemblies (solar-controlled glazing, low-emissivity glazing, heated windows, etc.), it is usual practice to deposit a thin-film multilayer comprising at least one functional layer on a substrate.

 When this functional layer (or these functional layers) is (or are) especially based on silver, it is necessary to deposit a silver layer (thickness between 8 and 15 nm) whose normal emissivity and/or electronic resistivity are minimal.

15 To do this, it is known that the silver layer must be deposited on an oxide sublayer which is :

- (i) made of perfectly crystallized zinc (wurtzite phase) with a preferred orientation formed by the basal planes ((0002) planes) parallel to the substrate ; and
- (ii) perfectly smooth (minimal roughness).

20 The current technical solutions for depositing the zinc oxide do not allow both these characteristics to be obtained.

 For example :

- the solutions for crystallizing zinc oxide (by heating the substrate, increasing the cathode power, increasing the thickness and increasing the oxygen content) result in an increase in the roughness of the layer, which leads to an appreciable degradation in the performance of the silver layer deposited on top ; and
 - the solutions for depositing a zinc oxide which is smooth or has a low roughness (low-pressure deposition, deposition on a very small thickness) result in partial amorphization of the silver layer, which impairs the quality of the heteroepitaxial growth of the silver on the ZnO.
- 30

 Within the context of the invention, it has been observed, surprisingly, that the deposition in particular of zinc oxide, but also of many other dielectrics, assisted by an ion beam coming from a linear source makes it possible, under certain conditions, to deposit a highly crystallized layer with an extremely low roughness.

35 This considerably improves the quality of the epitaxially grown silver layer on the

subjacent dielectric and therefore both the optical and mechanical properties of the multilayers.

Control Example 1

5 In this example, a zinc oxide layer 40 nm in thickness was applied to a glass substrate using an installation (10) illustrated in figure 1.

The deposition installation comprised a vacuum sputtering chamber (2) through which the substrate (1) ran along conveying means (not illustrated here), along the direction and in the sense illustrated by the arrow F.

10 The installation (2) included a magnetically enhanced sputtering system (5). This system comprised at least one cylindrical rotating cathode (but it could also have been a flat cathode), extending approximately over the entire width of the substrate, the axis of the cathode being placed approximately parallel to the substrate. This sputtering system (5) was placed at a height H5 of 265 mm above the substrate.

15 The material extracted from the cathode of the sputtering system was directed onto the substrate approximately as a beam (6).

The installation (2) also included a linear ion source (4) emitting an ion beam (3), which also extended approximately over the entire width of the substrate. This linear ion source (4) was positioned at a distance L4 of 170 mm from the cathode axis, in front of the cathode with regard to the direction in which the substrate runs, at a height H4 of 120 mm above the substrate.

The ion beam (3) was directed at an angle A relative to the vertical to the substrate passing through the axis of the cathode.

25 This deposition was carried out using a known sputtering technique on the substrate (1) running through a sputtering chamber (2) past a rotating cathode, based on Zn containing about 2% by weight of aluminum in an atmosphere containing argon and oxygen. The run speed was at least 1 m/min.

30 The deposition conditions given in Table 1a below were adapted so as to create a slightly substoichiometric zinc oxide layer with an index of 1.88 (whereas a stoichiometric ZnO layer has an index of 1.93 – 1.95).

This layer was analyzed by X-ray reflectometry in order to determine its density and thickness, and by X-ray diffraction in order to determine its crystallinity. The spectrum revealed a peak at $2\theta = 34^\circ$ typical of (0002) ZnO. The size of the

crystallites was deduced from the diffraction spectrum using the conventional Scherrer formula and using the fundamental parameters.

The light transmission through the substrate, the light reflection from the substrate and the resistance per square were also measured. The measured values are given in Table 1b below.

Example 1

In this example, a zinc oxide layer 40 nm in thickness was applied according to the invention to a glass substrate.

This deposition was carried out by sputtering onto the substrate, which ran through the same sputtering chamber as in Control Example 1, in an atmosphere at the sputtering cathode containing only argon. A linear ion source placed in the sputtering chamber was used to create, simultaneously with the sputtering, an ion beam using an atmosphere at the source composed of 100% oxygen. The source was inclined so as to direct the beam onto the substrate at an angle of 30°.

The modified deposition conditions made it possible to produce a zinc oxide layer having an index of 1.88, the density of which was identical to that of the control material.

The optical properties were barely affected by exposure to the ion beam.

The X-ray diffraction spectrum revealed a very intense ZnO (0002) peak showing, for constant ZnO thickness, an increase in the amount of ZnO that crystallized and/or a more pronounced orientation.

An iron constant of less than 1 at% was measured by SIMS.

Rutherford backscattering spectroscopy measurements showed that the ZnO layer contained 0.45 at% argon.

Table 1a

		Sputtering			Ion Source		
	Pressure	Power	Ar	O ₂	Energy	Ar	O ₂
Units	μbar	kW	sccm	sccm	eV	sccm	sccm
Cont. Ex. 1	0.8	3.0	80	70	--	--	--
Ex. 1	0.9	3.0	100	0	2000	0	80

Table 1b

	Properties						
	Density	Index	T_L	R_L	R_{\square}	ZnO Crystallite Size (nm)	
Units	g/cm^3		%	%	Ω / \square	Scherrer	Fund. Param.
Cont.	5.30	1.88	83.8	16.1	∞	17	15
Ex. 1							
Ex. 1	5.30	1.54	88.9	9.8	∞	12	12

Example 2

- 5 In this example, a glass substrate was coated with the following multilayer :
10 nm ZnO / 19.5 nm Ag / 10 nm ZnO,

where the lower zinc oxide layer was obtained as in Example 1 with exposure to an ion beam.

- 10 As in Example 1, the lower layer was produced by adapting the residence time of the substrate in the chamber in order to reduce the thickness of the oxide layer to 10 nm.

The substrate was then made to run past a silver cathode in an atmosphere composed of 100% argon and then once again past a zinc cathode in an argon/oxygen atmosphere under the conditions of Control Example 1.

- 15 This multilayer was analyzed by X-ray diffraction in order to determine its state of crystallization. The spectrum revealed a peak at $2\theta = 34^\circ$ typical of ZnO, and a peak at $2\theta = 38^\circ$ typical of silver. The size of the silver crystallites was determined from the diffraction spectrum using the conventional Scherrer formula and using the fundamental parameters.

- 20 The light transmission through the substrate, the light reflection from the substrate and the surface resistance were also measured.

The results are given in Table 2 below.

These properties are compared with those of a Control Example 2 in which the lower zinc oxide layer was produced without exposure to the ion beam.

- 25 The comparison reveals that the crystallization of the silver layer is considerably improved when the subjacent zinc oxide layer is produced with exposure to the ion beam, this being manifested by a lower surface resistance, i.e. an improved conductivity.

Table 2

	Properties				
	T _L	R _L	R _□	Ag Crystallite Size (nm)	
Units	%	%	Ω / □	Scherrer	Fund. Param.
Cont. Ex. 2	52.3	45.5	2.07	15.7	15.3
Ex. 2	58.6	40.7	1.86	17.4	17.6

Control Example 3

In this example, the following multilayer was produced on a glass substrate :

Substrate	SnO ₂	TiO ₂	ZnO	Ag	NiCr	SnO ₂
	15	8	8	10	0.6	30

- 5 in which the lower zinc oxide layer was obtained as in Example 1 with exposure to an ion beam.

The zinc oxide layer was produced as in Example 1 by adapting the residence time of the substrate in the chamber in order to reduce the thickness of the oxide layer to 8 nm.

- 10 Next, the substrate was made to run past a silver cathode in an atmosphere composed of 100% argon.

The optical and performance properties of Control Example 3 as single glazing (SG) and as double glazing (4/15/4 DG with the internal cavity composed of 90% Ar) are given in Table 3 below.

15

Example 3

- The same deposition conditions as those of Control Example 3 were used, except that a linear ion source was placed in the sputtering chamber and was used to create, simultaneously with the sputtering, an ion beam during production of the zinc-oxide-based layer, with an atmosphere at the source composed of 100% oxygen. The source was inclined so as to direct the beam onto the substrate at an angle of 30° and was positioned at a distance of about 14 cm from the substrate.

These modified deposition conditions made it possible to produce a zinc oxide layer having an index substantially identical to that of the control layer.

- 25 The optical and performance properties of Example 3 as single glazing (SG) and as double glazing (4/15/4 DG, the internal cavity of which was composed of 90% Ar) are also given in Table 3 below.

Table 3

		T_L (%)	R_L (%)	a^*	b^*	ϵ_n (%)	R_{\square} (Ω/\square)
Con. Ex. 3	SG	86	4.4	3.7	-7.8		
Con. Ex. 3	DG	77.4	11.6	0.7	-3.8	5.5	5
Ex. 3	SG	86.5	4.2	3.2	-7.7		
Ex. 3	DG	77.7	11.5	0.5	-3.8	5	4.5

As may be seen, the optical properties are barely affected by exposure to the ion beam, but the thermal properties are substantially improved, since a gain of 10% is obtained in terms of resistance per square (R_{\square}) and in normal emissivity (ϵ_n).

Control Example 4

A multilayer having the following layer thickness (in nanometers) was produced on a glass substrate, corresponding to the multilayer sold by Saint-Gobain Glass France under the brand name PLANISTAR :

Substrate	SnO ₂	ZnO	Ag	Ti	ZnO	Si ₃ N ₄	ZnO	Ag	Ti	ZnO	Si ₃ N ₄
	25	15	9.0	1	15	56	15	13.5	1	15	21

The optical and performance properties of Control Example 4 as double glazing (4/15/4, with the internal cavity composed of 90 % Ar) are given in Table 4 below.

Example 4

A multilayer having the same thicknesses as Control Example 4 was produced under the same conditions as those of Control Example 4, except that a linear ion source was placed in the sputtering chamber and used to create, simultaneously with the sputtering, an ion beam during production of each zinc-oxide-based layer directly subjacent to each silver-based functional layer.

The atmosphere at the source was composed of 100% oxygen. The source was inclined so as to direct the beam onto the substrate at an angle of 30° and was positioned at a distance of about 14 cm from the substrate. The energy of the ion beam was, for each pass, around 1000 eV. The pressure inside the chamber was 0.1 μ bar during the first pass and 4.3 μ bar during the second pass, for a target power of 5.5 kW during the first pass and 10 kW during the second pass.

These modified deposition conditions made it possible to produce a zinc oxide layer having an index substantially identical to that of the control layer.

The optical and performance properties of Example 4 as double glazing (4/15/4 the internal cavity of which was composed of 90 % Ar) are also given in Table 4 below.

As may be seen, the optical properties are barely affected by exposure to the ion beam, but the thermal properties are greatly improved, since again a gain of about 10% is obtained in terms of resistance per square (R_{\square}).

10

Table 4

	T_L (%)	λ_d (nm)	p_e (%)	R_{ext} (%)	L^*	a^*	b^*	SF (CEN)	U (W/m ² .K)	R_{\square} (Ω/\square)
Con. Ex. 4	71.8	553	2.6	12.0	41.2	-2.3	-1.7	42	1.17	2.7
Ex. 4	72.7	540	1.9	11.4	40.2	-2.7	-1.2	42	1.12	2.4

Example 5

The following multilayer was deposited : glass/Si₃N₄/ZnO (25 nm)/Ag (9 nm) and then the crystallographic characteristics of the zinc oxide and the electrical properties of the silver layer were measured. In addition, the RMS roughness of a ZnO(25 nm) glass not coated with silver and produced under the same conditions as previously was evaluated. The angle of inclination A of the ion source relative to the substrate was 30°. The measured values are given in Table 5 below.

20

Table 5

	Area of the ZnO (0002) Bragg peak (a.u.)	RMS roughness (nm) measured by AFM (25 nm thickness)	Resistance per square of a 9 nm thick silver film
ZnO without ion assistance	0	1.8	8.2
U = 1500 V	78	1.4	7.0
U = 3000 V	19	1.4	6.8

It may therefore be observed, surprisingly, that deposition of ZnO assisted by an ion beam makes it possible in the above multilayer to reduce the roughness of the layer thus deposited.

5 **Example 6**

TiO₂ monolayers were deposited on the glass with and without assistance by an ion source and then the roughness was measured by simulation of the optical properties (dispersion relationship) and by X-ray reflectometry. The angle of inclination A of the ion source relative to the substrate was 20°. The measured values
10 are given in Table 6 below.

Table 6

	Optical Roughness (nm)	X-ray RMS Roughness (nm)
TiO ₂ without ion assistance	1.7	1.5
U = 1000 V	0	0.5
U = 2000 V	0	0.7

The present invention has been described in the foregoing by way of example.
15 Of course, a person skilled in the art would be capable of producing various alternative embodiments of the invention without thereby departing from the scope of the patent as defined by the claims.